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(54) **UN PROCEDE DE PREPARATION D'UN COPOLYMER A  
BASE DE COMPOSES AROMATIQUES VINyliQUES ET DE  
DIENES CONJUGUES ET SON UTILISATION POUR LA  
FABRICATION DE VULCANISATS AYANT UN EXCELLENT  
COMPORTEMENT A L'AMORTISSEMENT**

(54) **A PROCESS FOR THE PREPARATION OF A COPOLYMER  
BASED ON VINYL AROMATIC COMPOUNDS AND  
CONJUGATED DIENES AND THE USE THEREOF FOR THE  
MANUFACTURE OF VULCANIZATES WITH OUTSTANDING  
DAMPING BEHAVIOR**

(57) According to the process of the invention, copolymers based on vinyl aromatic compounds and conjugated dienes with an average molecular weight ( $M_n$ ) from 50,000 to 600,000 g/mole, a vinyl aromatic compound content from 5 to 50 wt.% and a conjugated diene content from 50 to 95 wt.% are prepared by reacting a vinyl aromatic compound with a conjugated diene in the presence of a lithium metal-containing initiator, wherein polymerization is controlled such that the damping in the glass process encompasses a frequency range which is characterized in that the half width of the maximum of the loss factor  $\tan \delta$  is greater than 3 frequency decades.



**A PROCESS FOR THE PREPARATION OF A COPOLYMER BASED ON VINYL AROMATIC COMPOUNDS AND CONJUGATED DIENES AND THE USE THEREOF FOR THE MANUFACTURE OF VULCANIZATES WITH OUTSTANDING DAMPING BEHAVIOR**

ABSTRACT OF THE DISCLOSURE

According to the process of the invention, copolymers based on vinyl aromatic compounds and conjugated dienes with an average molecular weight ( $M_n$ ) from 50,000 to 600,000 g/mole, a vinyl aromatic compound content from 5 to 50 wt.% and a conjugated diene content from 50 to 95 wt.% are prepared by reacting a vinyl aromatic compound with a conjugated diene in the presence of a lithium metal-containing initiator, wherein polymerization is controlled such that the damping in the glass process encompasses a frequency range which is characterized in that the half-width of the maximum of the loss factor  $\tan \delta$  is greater than 3 frequency decades.

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**A PROCESS FOR THE PREPARATION OF A COPOLYMER BASED ON VINYL AROMATIC COMPOUNDS AND CONJUGATED DIENES AND THE USE THEREOF FOR THE MANUFACTURE OF VULCANIZATES WITH OUTSTANDING DAMPING BEHAVIOR**

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**FIELD OF THE INVENTION**

10 The present invention provides a process for the preparation of a copolymer based on vinyl aromatic compounds and conjugated dienes and the use thereof for the manufacture of vulcanizates with outstanding damping behavior, coupled with particularly good wet skid behavior and combined with good processability of the copolymers during the manufacture of corresponding vulcanizates.

15 **BACKGROUND OF THE INVENTION**

20 It is well known to improve the wet skid behavior (wet skid safety) of styrene-butadiene copolymers by increasing the breadth of dispersion of the vinyl content or of the styrene content. DE 31 15 878, EP 0 530 795 and EP 553 689 should be mentioned, in particular, in this connection. A disadvantage of the styrene-butadiene copolymers described in the patent publications mentioned is, in particular, the complicated method of preparation thereof, wherein it is important to ensure 1) that a particular temperature gradient is observed during the reaction or 2) that the amount of modifier or of monomers increases constantly during the reaction, entailing a  
25 special monitoring operation during polymerization.

**SUMMARY OF THE INVENTION**

30 The object of the present invention is to provide a simplified process for the preparation of copolymers based on vinyl aromatic compounds and conjugated dienes which does not require a particularly laborious monitoring of the monomers to

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be used, the temperature and the amount of modifier. Moreover, the copolymers and vulcanizates thereof should have improved wet skid behavior and outstanding damping behavior and good processing behavior during the manufacture of corresponding vulcanizates from the copolymers.

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#### DETAILED DESCRIPTION OF THE INVENTION

The present invention provides, therefore, a process for the preparation of copolymers based on vinyl aromatic compounds and conjugated dienes with an average molecular weight ( $M_n$ ) from 50,000 to 600,000 g/mole, a vinyl aromatic compound content from 5 to 50 wt.% and a conjugated diene content from 50 to 95 wt.%, which is characterized in that a vinyl aromatic compound is reacted with a conjugated diene in the presence of a lithium metal-containing initiator, polymerization being controlled such that the damping in the glass process encompasses a frequency range which is characterized in that the half-width of the maximum of the loss factor  $\tan \delta$  is greater than 3, preferably 3.5 to 6, more preferably 4 to 6 frequency decades.

Due to the continuously changing vinyl aromatic compound content in the polymer chain in the process according to the present invention, the damping behavior in the glass transition zone of the copolymer also changes. The damping behavior in the glass transition zone can then be characterized by measuring the half-width of the loss factor  $\tan \delta$ .

Frequency spectra of the complex shear modulus are prepared in order to determine the half-width of the loss factor  $\tan \delta$  (see, in this connection, the dissertation by C. Wrana, University of Ulm, 1996, p. 2-23). By applying the frequency/temperature superposition principle, the apparatus-related frequency range of the shear modulus spectra of the measuring device used may be extended to the relevant frequency range. From the maximum of the loss factor  $\tan \delta$ , which is caused by the glass relaxation process in the case of elastomers and can be found in a frequency range

The lithium metal-containing initiators are normally used in the process according to the present invention in amounts from 0.1 to 15 mmole, preferably 0.2 to 10 mmole, based on 100 g of polymer.

- 5 It may be advantageous for the process according to the present invention if alkali metal compounds are used in addition to the lithium metal-containing initiators.

The alkali metal compounds may be selected from alkali metal compounds according to the following general formulae:

10



wherein

- 15  $R^1, R^2, R^3, R^4$  and  $R^5$  is an alkyl group, a cycloalkyl group, an alkenyl group, an aryl group or a partially substituted group thereof, and  
M is Na, K, Rb or Cs.

- 20 Examples of an alkali metal compound having the formula  $R^1M$  include compounds such as methylsodium, ethylpotassium, n-propylrubidium, ethylcaesium, t-butylsodium, t-amylpotassium, n-hexylrubidium, 4-methylcyclohexyl sodium, 3-hexenylpotassium, 2,5-decadienylrubidium, 4,6-di-n-butyldecylsodium, phenylpotassium, benzylsodium and 4-tolylpotassium.

- 25 Alkali metal compounds having the formula  $R^2OM$  which may be used are alkali metal salts of mono- and polyhydric alcohols and phenols such as sodium, potassium, rubidium or caesium salts of methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, t-butyl alcohol, t-amyl alcohol, n-hexyl alcohol, cyclohexylalcohol, 2-butenyl alcohol, 4-methylcyclohexenyl alcohol, 3-cyclopentenyl alcohol, 3-hexenylalcohol, 2,5-decadienyl alcohol, allyl alcohol, 1,3-dihydrohexane, 1,5,9-trihydroxytridecane, benzyl alcohol, phenol, catechol,
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resorcinol, hydroquinone, pyrogallol, 1-naphthol, 2-naphthol, 2,6-di-t-butyl-4-methylphenol, 2,4,5,6-tri-t-butylphenol, n-nonylphenol and 1,12-dodecane diol.

5 Alkali metal compounds having the formula  $R^3COOM$  which may be used are alkali metal salts of mono- or polyvalent carboxylic acids such as sodium, potassium, rubidium or caesium salts of lauric acid, myristic acid, palmitic acid, stearic acid, arachidic acid, linoleic acid, linolenic acid, phenylacetic acid, benzoic acid, sebacic acid, phthalic acid and 1,8,16-hexadecanetoloyl carboxylic acid.

10 Alkali metal compounds having the formula  $R^4R^5NM$  which may be used are alkali metal salts of secondary amines such as sodium, potassium, rubidium or caesium salts of dimethylamine, di-n-butylamine, methyl-n-hexylamine, di-(3-hexenyl)amine, diphenylamine and dibenzylamine.

15 Alkali metal-containing alcoholates are used in preference in the process according to the present invention, such as sodium, potassium, rubidium or caesium salts of methyl alcohol, ethyl alcohol, n-propyl alcohol, isopropyl alcohol, tert.-butyl alcohol, tert.-amyl alcohol, n-hexyl alcohol, cyclohexylalcohol, butyl alcohol, phenol and 1-naphthol. More particularly preferably, the potassium salt of tert.-amyl alcohol is  
20 used.

The alkali metal compounds are normally used in the process according to the present invention in an amount such that the molar ratio of lithium metal-containing initiator to alkali metal compounds is 1 : 0.005 to 1 : 0.25.

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Of course, it is also possible to carry out the process according to the invention in the presence of so-called modifiers such as ethers and/or amine compounds such as tertiary amines, which are capable of controlling the vinyl content in the polymer chain. More particularly, ether compounds and amine compounds which may be  
30 mentioned include triethylamine, pyridine, tetramethylethylene diamine (TMEDA), tetrahydrofuran (THF), diethylether, diphenylether, anisole, ethylene glycol

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dimethylether, ethylene glycol diethylether, ethylene glycol ethyl-tert.-butyl ether, 2,2-bis-(2-oxolanyl)propane, and oligomeric oxolanyl alkanes. The modifiers mentioned may be used both individually and in mixture.

5 The optimum amount of modifiers to be used may be determined easily by appropriate preliminary tests and depends on the desired vinyl group content in the polymer chain. Amounts from about 0.005 to 400 mmole per 100 g of monomers used are customary.

10 The process according to the present invention may be carried out at temperatures from about 40°C to 160°C, preferably 50°C to 130°C. The process according to the present invention may be carried out at a pressure below atmospheric, at normal pressure and at elevated pressure, preferably at elevated pressure, for example, at pressures from 1 to 10 bar.

15 The process according to the present invention may be carried out both continuously and batchwise.

20 The process according to the present invention is carried out in the presence of the conventional inert solvents which are well known for anionic polymerization. These are, more particularly, aromatic and/or aliphatic hydrocarbons with 2 to 12 carbon atoms, such as ethane, propane, iso- and n-butane, iso- and n-pentane, iso- and n-hexane, iso- and n-heptane, iso- and n-octane, cyclobutane, cyclopentane, cyclohexane, cycloheptane, cyclooctane, where n-hexane and cyclohexane are preferable.

25 The solvents may be used both individually and in mixture, and of course in the form of their isomer mixtures.

30 The most favourable amount of solvent in each case may also be determined easily by appropriate preliminary tests.

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The copolymers prepared according to the present invention based on aromatic vinyl compounds and conjugated dienes are suitable for the manufacture of vulcanizates which have outstanding damping behavior coupled with superior wet skid behavior, which is why the copolymers prepared according to the present invention are particularly suitable for the manufacture of tires, preferably tire treads. Of course, other vulcanized molded articles in which the above-mentioned physical properties are of importance may be manufactured from the copolymers according to the present invention.

## 10 EXAMPLES

The polymerization reactions were carried out under nitrogen with the exclusion of air and moisture.

15 The determination of the styrene content in the polymer and of the selectivity of polybutadiene (1,4-cis, 1,4-trans and 1,2-content) is carried out by IR spectroscopy, the damping behavior and the determination of the half-width of the loss factor by frequency-dependent measurements of complex material quantities.

## 20 Examples 1 to 4

### Polymerization

Polymerization was carried out in a 2 liter Büchi glass autoclave with stirrer and jacket heating. The amounts of styrene, 1,3-butadiene, hexane (mixture of isomers), initiator solution (n-butyllithium in n-hexane), alkali metal alcoholate potassium-tert.-amylate (KTA) and modifier diethoxyethane (DEE) given in Table 1 were added under nitrogen. The temperature was set at 60°C. After complete conversion had been achieved (about 2 h), the polymer was isolated by precipitation of the polymer solution in ethanol/BHT (2,6-di-tert.-butyl-4-methylphenol) and dried at 60°C in a



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Table 2:      Examples 5 to 8

Example	5	6	7	8
<u>Polymerization</u>				
BuLi in mmoles	1.25	1.25	1.25	1.25
Hexane in g	850	850	850	850
Styrene in g	37.5	37.5	37.5	37.5
1,3-butadiene in g	112.5	112.5	112.5	112.5
KTA in mmoles	0	0.063	0.125	0.25
<u>Polymer</u>				
Styrene content in wt.%	25.5	26.2	26.4	26.1
Butadiene content in wt.%	74.5	73.8	73.6	73.9
cis in %	30.0	28.7	27.4	25.6
trans in %	37.4	35.9	34.4	32.4
1,2- in %	7.1	9.2	11.8	15.9
Half-width in log (f/Hz)	4.4	4.3	3.7	5.0
Frequency position in log (f/Hz)	6.9	6.5	6.0	5.6

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7. A process according to Claim 1, wherein the vinyl aromatic compound content is in the range from 10 to 45 wt.%.

8. A process according to Claim 1, wherein the conjugated diene content is in the range from 55 to 90 wt.%.

5 9. A process according to Claim 1, wherein said polymerization is carried out at temperatures from 40°C to 160°C.

10. A process according to Claim 1, wherein said polymerization is carried out at temperatures from 50°C to  
10 130°C.

11. A process according to Claim 1, wherein said polymerization is carried out in the presence of an inert solvent.

12. A process according to Claim 1, wherein said  
15 polymerization is carried out in the presence of alkali metal compounds.

13. A process according to Claim 12, wherein the alkali metal compounds are of the following general formulae:  $R^1M$ ,  $R^2OM$ ,  $R^3COOM$  and  $R^4R^5NM$ , wherein  $R^1$ ,  $R^2$ ,  $R^3$ ,  $R^4$  and  $R^5$  is an  
20 alkyl group, a cycloalkyl group, an alkenyl group, an aryl group or a partially substituted group thereof, and M is Na, K, Rb or Cs.

14. A process according to Claim 12, wherein the molar ratio of alkali-metal compounds to lithium metal-containing initiator is 0.005:1.

15. A process according to Claim 12, wherein the molar ratio of alkali-metal compounds to lithium metal-containing  
25 initiator is 0.25:1.

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